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EFFECT OF SYNTHESIZING PARAMETERS ON MORPHOLOGY AND DIAMETER OF CARBON NANOTUBES GROWN BY THERMAL CVD METHOD

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ABSTRACT

Carbon nanotubes were synthesized by thermal chemical vapor deposition method. There were parameters of the synthesizing process which influence the morphology and quality of nanotubes such as substrate material, the topology of substrates, the reduction process, and growing temperature. The topology of substrate affected the uniform of nanotubes. The reduction process using NH_3 reductant helped reducing diameter of carbon nanotubes. Growing temperature complexly modified the quality of carbon nanotubes.

Keywords: carbon nanotubes, thermal CVD, VLS mechanism.

1. INTRODUCTION

Carbon nanotubes (CNTs) were discovered by Iijima in 1991. This discovery has triggered a lot of researches on growth and application of CNTs [1]. Although CNTs have been studied for almost 25 years, they are still an attractive subject because of their outstanding structural and physical properties as well as potential applications [2-6]. CNT pillars were synthesized for biosensor application in microfluidic devices [2]. CNTs were synthesized for fabricating composite film for aero application [4]. Strong cable was expected to be weaved from very long CNTs [5], and CNTs were grown with high quality in low temperature (below 600 ^oC) in different substrates for designed applications [6, 7].

Numerous methods have been used to synthesize CNTs such as laser ablations, plasma enhanced chemical vapor deposition, thermal chemical vapor deposition, etc. But the most used method is Thermal Chemical Vapor Deposition (TCVD) method because of its simple experimental setup. In TCVD method, the decomposition reaction of precursors is used to provide carbon source for CNT growth with an assistance of metallic nanoparticles play as the seed. These metal catalyst nanoparticles play a very important role in the growing process of CNTs following Vapor-Liquid-Solid (VLS) mechanism. The growing process of CNTs is

divided into four stages: (1) the formation of catalytic nanoparticles from initial metallic thin film; (2) the decomposition of carbon precursor gas to provide source of carbon atoms; (3) carbon atoms get to and penetrate into catalytic nanoparticles, then make carbide compound with catalytic metal; (4) when carbon get to supersaturating stage in carbide compound, it will be extracted out of metal to create graphite layer around surface of catalytic particle to form CNT [8]. Following VLS mechanism, the formation and morphology of CNTs strongly depend on metal catalyst, substrate temperature, reaction temperature, the partial pressure of precursors and the volume rate of precursor.

In this paper, we report effects of synthesizing parameters of TCVD method on the formation of CNTs. Acetylene (C_2H_2) was used as the carbon precursor; used metal catalyst is permalloy ($Fe_{19}Ni_{81}$); reduction agent of metal catalyst is ammonia gas (NH_3). The morphology of CNTs was investigated by Field Emission Scanning Electron Microscopy (FESEM). The effect of substrate's topology, pretreating process of catalytic metal with NH_3 and growing temperature on morphology and formation of CNT will be discussed.

2. EXPERIMENTAL

CNT was synthesized by TCVD method in horizontal furnace using quartz tube chamber. The setup of experiment is shown in Figure 1.a. The substrates are of 2x1 cm^2 size. To investigate the effect of substrate topology, we used two types of substrate: SiO_2/Si and Al_2O_3. On these substrates, Pt electrodes were patterned by photolithography (SiO_2/Si) or screen-printing technique (Al_2O_3).

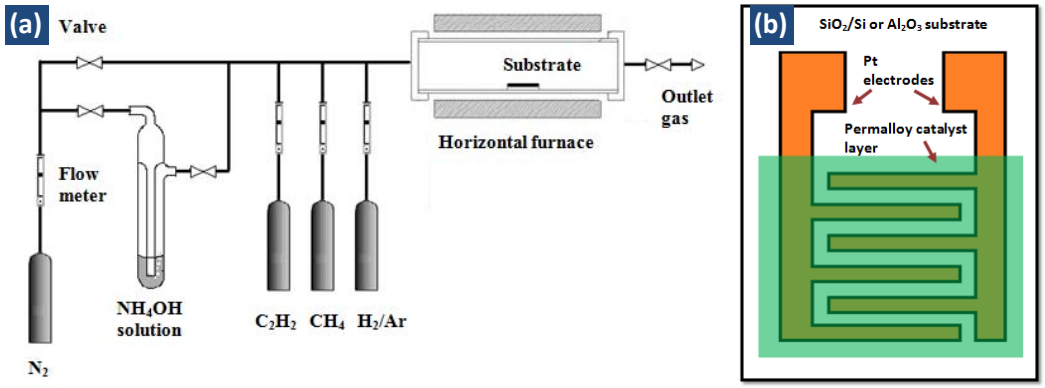

Figure 1. The schematic of TCVD system with a horizontal furnace to synthesize CNTs (a) and the illusion of substrate with patterned Pt electrodes permalloy catalyst layer (b).

Permalloy catalyst thin film was sputtered on substrates as shown in the Figure 1.b. The thickness of catalyst thin film was measured by Quartz Crystal Microbalance (QCM) integrated into sputtering system. In this paper, CNTs was grown with two different permalloy thin film thickness: 7 nm, 10 nm. Nitrogen gas was used to create an inert environment in chamber in both heating, reaction, and cooling processes. Nitrogen also was used to move exhausted gas out of the chamber. After the substrate was heated up, NH_3 was brought into chamber by letting N_2 gas go through NH_4OH solution to reduce the oxide layer formed on top catalyst film. Then C_2H_2 was put on to grow CNT. The detail of synthesis process can be found elsewhere [9,10]. The morphology and diameter of CNTs were investigated by Field Emission Scanning Electron Microscopy (FESEM).

3. RESULTSAND DISCUSSION

3.1. Effect of topology of substrate

According to VLS mechanism, the formation of catalytic nanoparticle keeps vital role in the formation of CNTs. Many parameters can affect the formation of catalytic nanoparticles such as substrate temperature, the thickness of catalyst thin film, the type of catalytic metal, etc. In this report, we aim to focus on the role of interaction between topology of substrate and catalyst layer into the formation of catalytic nanoparticles. Two substrates which have very different topologies: SiO_2/Si (smooth surface) and Al_2O_3 (roughly surface) were used to support CNTs growth [11].

Figure 2 shows FESEM image of CNTs grown on SiO_2/Si substrate (Figure 2.a) and on Al_2O_3 substrate (Figure 2.b) in the same growing conditions (temperature, catalyst layer – 7-nm permalloy thin film, etc.). We can see the difference between morphology of CNTs in two samples. CNTs grown on SiO_2/Si substrate have uniform size with straight and smooth walls. CNTs grown on Al_2O_3 are curlier and not uniform. In the former case, CNTs have and average diameters of ~ 70 nm. In the later case, there is bimodal distribution of CNTs which have average diameters of CNTs on top and below layers are ~ 70-nm and ~ 100-nm, respectively. This difference of diameter distribution and morphology of CNTs are explained by the different topologies of two substrates. Al_2O_3 substrate has rougher surface which acts as multi-valley surface isolating catalytic particles. The size of catalytic particles is determined by the size of valley instead of determined by itself as on smooth SiO_2/Si surface [12]. Moreover, because of the isolation of CNTs on Al_2O_3 valleys, the physical interaction (Van de Waals force) between CNTs in growing stage is weaker than that of CNTs grown on SiO_2/Si substrate. The weaker interaction causes CNTs on Al_2O_3 substrate be curlier and less well-aligned than CNTs grown on SiO_2/Si substrate.

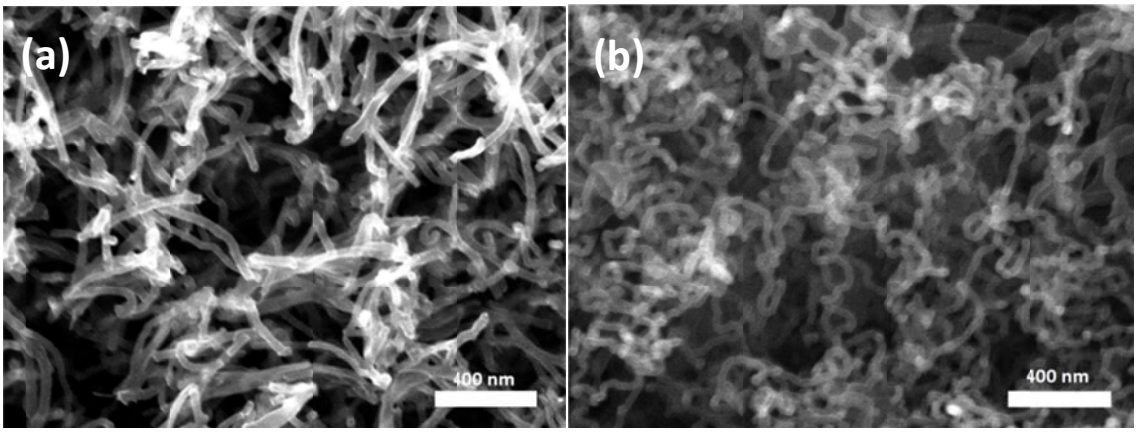

Figure 2. FESEM images of CNT grown on SiO_2/Si substrate (a) and Al_2O_3 substrate (b) at 750 ^oC.

The effect of topology of substrate was also showed through the interaction between metal catalyst, electrode layer, and substrate. In the sputtering process to prepare catalyst layer, permalloy was sputtered on both substrate (area between electrodes) and on Pt electrodes. In the growing process, permalloy interacted with Pt electrodes differently depending on substrate. On SiO_2/Si substrate, because of smooth surface, Pt electrodes did not support permalloy to form suitable cluster for CNTs growth that causes no CNTs grown on Pt electrodes. CNTs only grew

on area between electrodes (Figure 3.a). In contrary, on Al_2O_3 substrate, CNTs were observed on both Pt electrodes and area between electrodes. This is because Pt electrodes acted as a supporting layer which interacted with permalloy to create suitable catalytic particles for CNTs growth [7, 13]. On electrodes, the obtained products were not only CNTs (~ 200 nm in diameter) but also spring-like carbon which illustrated the complex interaction between permalloy and Pt electrodes on Al_2O_3 substrate (Figure 3.b). We also observed the same results with Au electrodes.

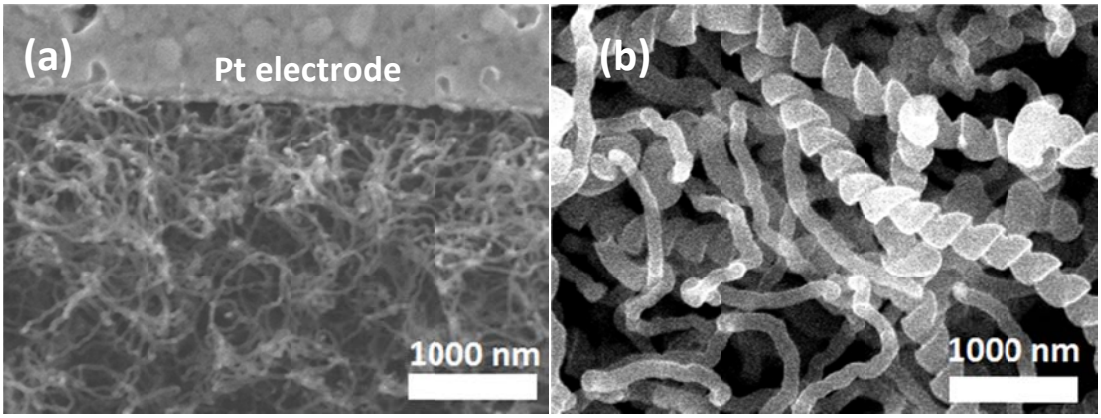

Figure 3. FESEM images of CNTs grown between instead of on the Pt electrodes on SiO_2/Si substrate (a), and CNTs and other spring-like carbon grown on Pt electrodes on Al_2O_3 substrate (b) at 750 ^oC.

3.2. The effect of reducing agent NH3

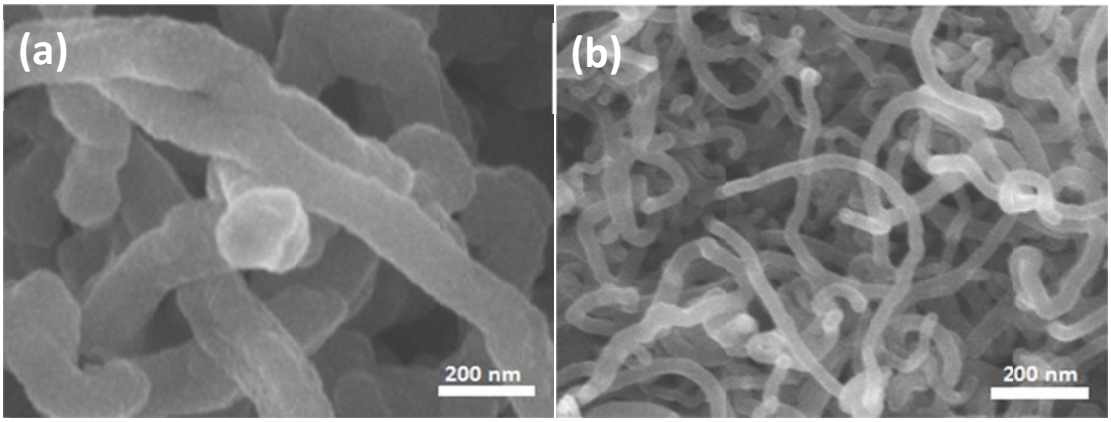

Figure 4. FESEM images of CNTs grown with 10-nm permalloy catalyst layer on SiO_2/Si substrate at 750 ^oC: no using reducing agent NH_3 (a) and using NH_3 (b).

Ammonia (NH_3) gas was used to reduce the metal oxide layer inevitably covering on top of catalyst layer. NH_3 was transferred into reaction chamber by flowing N_2 gas through NH_4OH solution. The reduction process was carried out before putting carbon precursor into chamber for decomposition.

The FESEM images of CNTs grown at 750 ^oC without and with using NH_3 gas are shown in Figure 4. The difference of CNTs morphology between two cases is clearly presented.

Without using NH_3 gas (Figure 4.a), the obtained CNTs have larger diameter (~150 nm), less smooth walls. On the walls of CNTs, qualitatively, there are many disorder carbons which cause less smoothness. With using NH_3 gas (Figure 4.b), CNTs have smaller diameter (~ 50 nm), smoother, longer and straighter walls. The reason is because of the appearance of natural metal oxide layer cover catalyst layer which both restricts diffusion of catalytic metal atoms and deactivates the catalytic properties of metal. The metal oxide has higher melting temperature than metal, so at high temperature (in the range from 600 ^oC to 900 ^oC), it formed a solid layer over catalyst layer preventing metal atoms diffusing on substrate to make smaller particles.

With using NH_3 reductant, the passive oxide layer was reduced into active metal which supporting catalytic activity particles.

$$2yNH_3 + 3Fe_xO_y \xrightarrow{t^o} 3xFe + 3yH_2O + yN_2 \quad (1)$$

$$2NH_3 + 3NiO \xrightarrow{t^o} 3Ni + 3H_2O + N_2 \quad (2)$$

The removing of passive oxide layer also permits catalytic metal atoms to diffuse and form smaller nanoparticles.

Without using NH_3 reductant, when C_2H_2 was transferred into chamber, there was still a solid oxide layer cover catalytic nanoparticles. So the nanoparticles not only had large dimension but also had passive surface which prevented carbon atoms to penetrating into metallic particles at the first stage. When decomposition of C_2H_2 happened, oxide layer was reduced into metal by by-product of decomposition as following reactions:

$$C_2H_2 \xrightarrow{t^o} 2C + H_2 \quad (3)$$

$$H_2 + NiO \xrightarrow{t^o} Ni + H_2O \quad (4)$$

$$yH_2 + Fe_xO_y \xrightarrow{t^o} xFe + yH_2O \quad (5)$$

These reactions occurred simultaneously with the formation of carbon layer on catalytic particle, so the penetration of carbon into newborn metal was harder in compare with the case using NH_3. These processes supported CNTs to grow but with larger diameter and they had more disorder carbon on the walls. These results are agreeable with the explanation of Hart et al. [8] and Campbell et al. [14]. We observed the similar results when using mixer of H_2/Ar gas to reduce metal oxide layer before decomposing C_2H_2.

3.3. Effect of growing temperature

Growing temperature or reaction temperature affects complexly to the formation and morphology of CNTs synthesized by TCVD method [8,9,14]. The reaction temperature varies the rate of decomposition, and then modifies the rate of supplying carbon atoms for CNTs' seed –catalytic nanoparticles [8]. It is reported that the faster carbon feedstock supply rate resulted in straighter and smoother CNTs [8, 14]. Our results deduced more complex influence of reaction temperature.

Figure 5 showed FESEM images of CNTs grown at different temperatures: 500 ^oC, 600 ^oC, 700 ^oC and 750 ^oC on SiO_2/Si substrate. These images show that, at higher growing temperature, especially at 750 ^oC, the obtained CNTs are more well-aligned, straighter, and smoother. However, when the growing temperature get higher (to 800 ^oC, 850 ^oC), the CNTs conversely

are curlier. At 900 ^{o}C and higher growing temperature, we did not observe the formation of CNT (we did not show here).

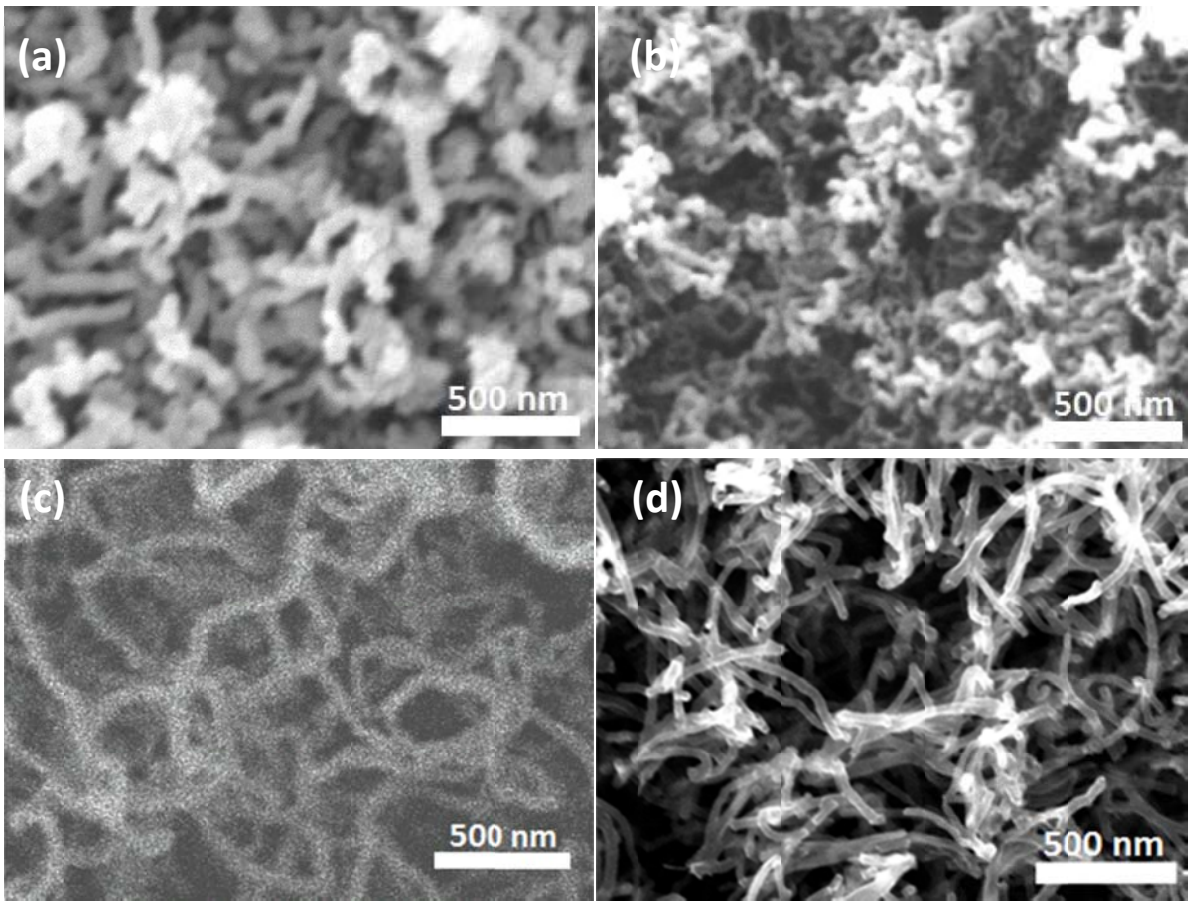

Figure 5. FESEM images of CNTs grown at different temperatures: (a) 500 ^{o}C, (b) 600 ^{o}C, (c) 700 ^{o}C and (d)750 ^{o}C on SiO_2/Si substrate with 7-nm permalloy catalyst layer.

This complex behavior is explained by the decomposition rate of C_2H_2. The ratio of C_2H_2 and N_2 was kept constant (50 sccm C_2H_2/400 sccm N_2) in all our experiments. At 750 ^{o}C, this ratio gives the favorable supply feedstock carbon for CNTs growing. At lower temperature (in the range of 500 ^{o}C to 700 ^{o}C), the decomposition rate of C_2H_2 is lower causing the reduction of growing rate of CNTs and less well-aligned, less smooth-wall CNTs. At higher temperature (higher than 750 ^{o}C), the decomposition reaction occurs faster causing the production of carbon increase fiercely. The rate of supplying carbon is much more than the penetration rate of carbon into catalytic nanoparticles. The excess carbon atoms which could not get into catalytic nanoparticles will aggregate to form graphitic carbon layer covering catalytic nanoparticles or CNTs' walls. This layer causes CNTs become curlier and less smooth. At 900 ^{o}C, a very thick layer of graphitic carbon was immediately formed just after C_2H_2 appearance. This graphitic carbon layer deactivated the catalytic properties of metal nanoparticles that restrict the formation of CNTs.

4. CONCLUSIONS

We have shown the effect of substrate's temperature, reducing process of metal catalyst oxide and reaction temperature on the formation of CNT grown by TCVD methods. The topology of substrate is more even; the obtained CNTs are more uniform and well-aligned. The using NH3 to treat the passive oxide layer on the catalytic film not only makes catalyst film active, but also helps create smaller catalytic particles. The CNTs grown from these particles, then, are smaller, smoother and have less amorphous carbon on the walls. The reaction temperature complexly influences on the formation of CNT. With C_2H_2 precursor, as the reaction temperature is higher (in the range from 500 ^oC to 750 ^oC), the decomposition reaction occurs faster, and the catalytic activity of metal nanoparticles are higher. These facts together provoke CNTs to grow faster, well-aligned, more uniform and smoother. When reaction temperature gets higher than 750 ^oC, C_2H_2 decomposes fiercely causing quality of CNTs is lower.

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TÓM TẮT

ẢNH HƯỞNG CỦA CÁC ĐIỀU KIỆN CHẾ TẠO TỚI HÌNH THÁI VÀ ĐƯỜNG KÍNH CỦA ỐNG NANÔ CÁCBON MỌC BẰNG PHƯƠNG PHÁP CVD NHIỆT

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Ống nanô cácbon được tổng hợp bằng phương pháp lắng đọng nhiệt hóa học từ pha hơi. Trong phương pháp này, có các thông số hay điều kiện chế tạo ảnh hưởng tới hình thái, đường kính và chất lượng của ống nanô cácbon như: vật liệu đế, tô pô bề mặt đế, quá trình khử kim loại xúc tác và nhiệt độ mọc. Tô pô hay độ mấp mô bề mặt đế ảnh hưởng tới độ đồng đều của ống nanô. Quá trình khử sử dụng tác nhân khử NH_3 giúp làm giảm đường kính của ống nanô cácbon. Nhiệt độ mọc ảnh hưởng phức tạp tới chất lượng của ống nanô cácbon.

Từ khóa: ống nanô cácbon, CVD nhiệt, cơ chế VLS.